Njuguna, Michael and Yan, Cheng and Bell, John M. and Yarlagadda, Prasad K. (2009) ***AC/DC electrical characteristics of epoxy-multi wall carbon nanotube nanocomposites***. In: Proceedings of the 6th International Conference on Precision, Meso, Micro and Nano Engineering, 11-12 December 2009, Coimbatore, India.

AC/DC electrical characteristics of epoxy-multi wall carbon nanotube nanocomposites

M. K. Njuguna[#], C. Yan[*], J. M. Bell[†] and P. Yarlagadda[‡]

*Research Student, *Associate Professor,
School of Engineering,
Faculty of Built Engineering and Environment
Queensland University of Technology,
Brisbane, QLD 4001, Australia
E-mail: #m.njuguna@qut.edu.au
*c2.yan@qut.edu.au

†Professor & Assistant Dean (Research)
‡Professor & Director (Smart Systems)
Faculty of Built Engineering and Environment
Queensland University of Technology,
Brisbane, QLD 4001, Australia
†j.bell@qut.edu.au
‡y.prasad@qut.edu.au

Abstract: Epoxy nanocomposites with multiwall carbon nanotubes (MWCNTs) filler up to 0.3%wt were prepared by shear mixing and good dispersion of the MWCNTs in the epoxy was successfully achieved. The electrical behaviour was characterized by measurements of the alternating current (AC) and direct current (DC) conductivities at room temperature. Typical percolation law behaviour was observed with a low percolation threshold of 0.055%. Frequency independent AC conductivity was observed at low frequencies but not at high frequencies. An equivalent circuit models was used to predict the impedance response in these nanocomposites.

Keywords: multi walled carbon nanotubes, nanocomposites, conductivity

1.0 INTRODUCTION

Carbon nanotubes (CNTs) have excellent electrical, mechanical and electromechanical properties. When incorporated into polymers, high electrical conductivity can be achieved in the formed nanocomposites even at very low CNT volume fraction (often below 1% wt). In addition, the electrical conductivity of the CNT nanocomposites is sensitive to mechanical strain, resulting in potential applications for strain sensing (Kang, Schulz et al. 2006; Pham, Park et al. 2008; Anand and Mahapatra 2009), electromagnetic interference shielding (Li, Huang et al. 2006), electrostatic dissipation (Yu, Hu et al. 2006) and photovoltaic devices (Kymakis and Amaratunga 2002). The electrical behaviour of CNT based polymer nanocomposites has been extensively explored with emphasis on several aspects, such as insulator-conductor transition (percolation threshold) and the relationships between conductivity and function of filler volume ratio, CNT orientation and dispersion, CNT treatment and processing conditions (Bumsuk Kim, Jongjin Lee et al. 2003; Sandler, Kirk et al. 2003; Schmidt, Kinloch et al. 2007; Hu, Masuda et al. 2008). In general, the electrical behaviour of polymer/CNT composites can be explained according to percolation theory and tunneling effect. However, despite broad investigation on CNT polymer nanocomposites, fundamental understandings of these properties are still lacking, such as percolation mechanism. Also, the effects of thermal strain, loading modes and CNT functionalization on the electromechanical response are yet to be fully elucidated. To this end, further experimental and theoretical investigations are needed. In this work, multi-walled CNT/polymer nanocomposites were successfully fabricated. Their electrical behaviour, in particular the conductivity under DC (direct current) and AC (alternating current) conditions were investigated.

2.0 MATERIALS AND EXPERIMENTAL PROCEDURE

2.1 Materials and fabrication of nanocomposites

Chemical vapour deposition (CVD) synthesized MWCNTs were used as supplied. The purity of the MWCNTs was more than 99.5%, diameter was between 30 – 70nm while the length ranged from 4 - 6μm. The epoxy chosen for this study was an unmodified diglycidyl ethyl of Bisphenol A (DGEBA) epoxy resin cured using piperidine. Polymer nanocomposites with MWCNT content between 0-0.3%wt were prepared. The epoxy/MWCNT mixture was mixed using a planetary shear mixer (Thinky

Mixer) and degassed in a vacuum oven. Samples were obtained by curing the epoxy/CNT/hardener mixture at 120°C for 16h.

2.2 Microanalysis

The CNTs and nanocomposites were observed using scanning electron microscopy (FEI Quanta 200 Environmental SEM). To examine the dispersion of the CNTs with the epoxy matrix, the cured samples were fractured and then observed using the SEM. The morphology of the MWCNTs was also examined using transmission electron microscopy (TEM, JEOL TEM-2010) with an acceleration voltage of 160 kV. The TEM samples were prepared by shear mixing small amounts of nanotubes in ethanol, drop casting the mixture on a carbon coated copper grid and finally evaporating the ethanol.

2.3 Measurement of conductivity

Impedance measurements were carried out at room temperature using a Princeton Applied Research Model 273A Potentiostat coupled with a lock in amplifier (Model No. 5210). The parameters chosen for the tests included a frequency range of 100 mHz – 100 kHz, AC amplitude of 10 mV rms, and a DC potential of 0.0 V, three samples for each MWCNT content (%wt) were tested. Impedance data was acquired using PowerSuite Software. DC resistance measurements were carried out using a Fluke 45 Digital multimeter; six samples for each MWCNT content were tested. The samples were silver coated to reduce contact resistance and then pressure-sandwiched between two copper electrodes to assure excellent contact between the electrodes and the samples.

3.0 RESULTS AND DISCUSSION

3.1 Morphology and dispersion of MWCNTs in epoxy

The TEM and SEM images of the MWCNTs are shown in Fig. 1 and 2, respectively.

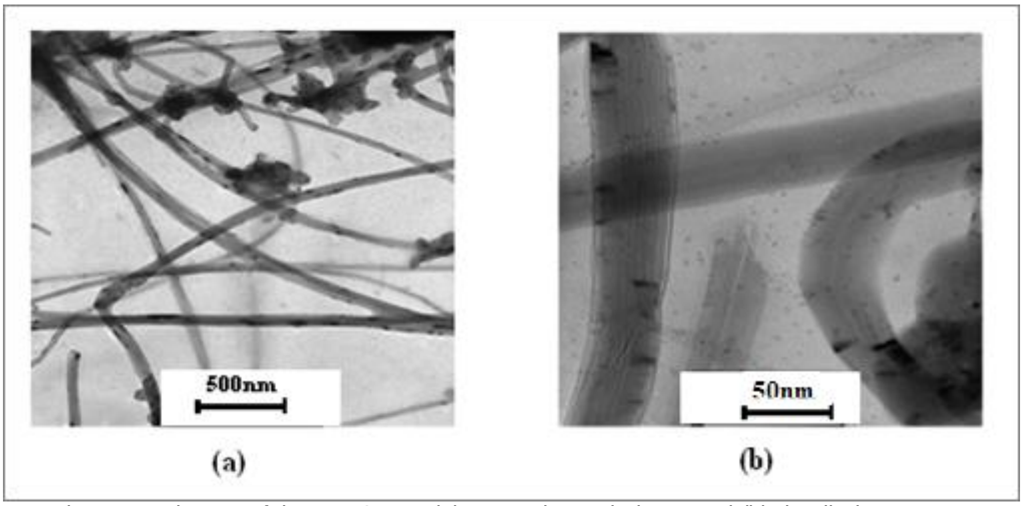


Fig. 1 TEM image of the MWCNTs: (a) general morphology, and (b) detailed structures

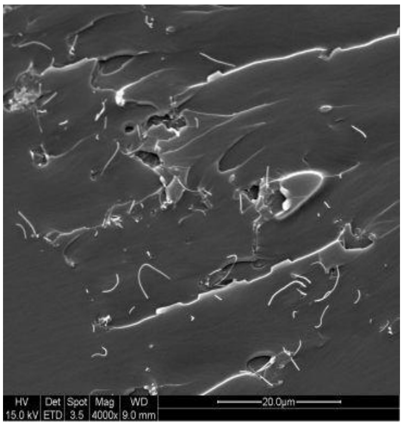
The general morphology of the MWCNTs is shown in Fig 1(a). Most of the MWCNTs are straight in shape and no obvious entanglement can be observed. Fig. 1 (b) shows the detailed structures of the MWCNTs, including the multiply walls and the central core. The MWCNTs used in this study were produced by a CVD process and annealed at 2600°C. The annealing significantly improved the quality of the CNTs. An even dispersion of MWCNTs in the epoxy matrix corresponding to low and high nanotube contents can be observed in Fig. 2.

3.2 DC and AC electrical conductivity

In general, the electrical conductivity of conductor-insulator heterogeneous mixtures can be described by a percolation function,

$$\sigma = \sigma_o(\varphi - \varphi_c)^t \quad \text{.....(1)}$$

where φ is the fraction of the conductor, φ_c is the percolation threshold concentration and *t* is the critical exponent. According to classical percolation theory, the critical exponent t, is dependent only on dimensionality and for three-dimensional systems, t ≈ 2 (Stauffer 1985).



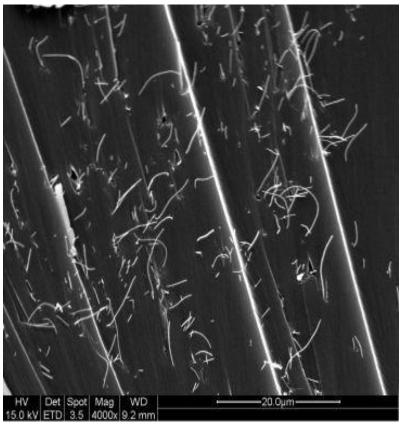
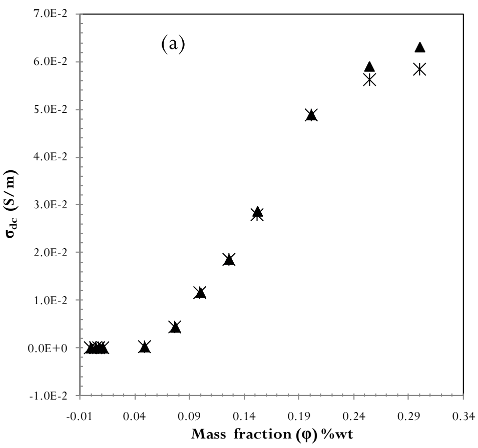


Fig. 2 Dispersion of MWCNTs in epoxy matrix: (a) 0.1%wt CNT and (b) 0.254%wt CNT.

The percolation threshold is determined by factors such as conductor type and shape, conductivities of conductor and insulator, dispersion and processing parameters. In this work, all resistance measurements were taken at room temperature. As shown in Fig. 3(a), both DC and AC conductivity demonstrate the typical percolation behaviour. To obtain the critical exponent t and the percolation threshold φ_c, a log-log plot of the conductivity data was prepared (Fig. 3(b)).



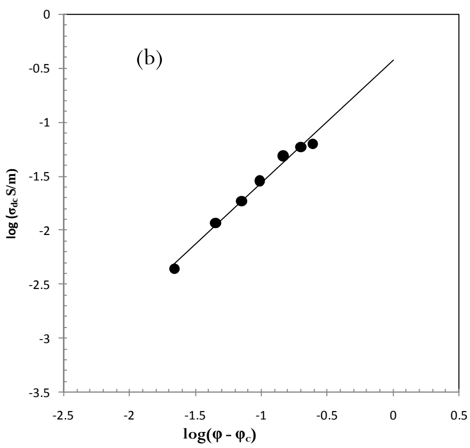


Fig. 3 (a) DC (▲) and ac electrical (*) conductivities as a function of nanotube content, and (b) log-log plot of conductivity against ($\varphi - \varphi_c$).

t = 1.14± 0.2 and φ_c = 0.055 ± 0.01%wt were obtained through linear regression. Also, conductivity of 6 x 10^{-2} S/m corresponded to the nanotube content of 0.3%wt. The percolation threshold obtained in this work falls within the range (0.0021 – 0.7%wt) reported for many epoxy-MWCNT epoxy nanocomposites(Bauhofer and Kovacs 2009) and is very similar to the of work by Hu et al (Hu, Masuda et al. 2008) in which similar MWCNTs and fabrication method were adopted. As mentioned before, the percolation threshold in polymer-CNT nanocomposites is dependent on materials and processing conditions, such as CNT dispersion and even CNT aspect ratio (Li, Ma et al. 2007). The aspect ratios are in the range 85-200 for the MWCNTs used in this study. The low percolation threshold obtained in this study may also be attributed to excellent dispersion, and high structural integrity of the MWCNTs used, as shown in Figs. 1 and 2. On the other hand, the AC conductivity of the nanocomposites is shown in Fig. 4.

In Fig. 4(a), when nanotube content is below the percolation threshold ($\varphi < \varphi_c$) there is a distinct high frequency dependent behaviour, in contrast to the frequency independent conductivity at low frequencies. At nanotube contents above the percolation threshold ($\varphi > \varphi_c$) the conductivity is independent of the frequency and remains almost constant with a slight increase at high frequencies. The behaviour is confirmed again in Fig 4 (b) where a log-log plot of the impedance moduli vs angular frequency is illustrated. This AC conductivity behaviour at different frequencies is typical for disordered insulator-conductor mixtures, with a transition from a frequency dependent conductivity at high frequencies to a frequency independent conductivity at low frequencies. At high frequencies, conductivity scales with frequency according to an approximate power law $\sigma(\omega) = \omega^s$ (Kilbride, Coleman et al. 2002). The exponent *s* can be estimated from a consideration of the composite conductivity at nanotube contents lower than the percolation threshold using the relationship (McLachlan, Chiteme et al. 2005),

$$\sigma_n = \sigma_i \left(\frac{\varphi_c}{\varphi_c - \varphi} \right)^S \quad \text{...(2)}$$

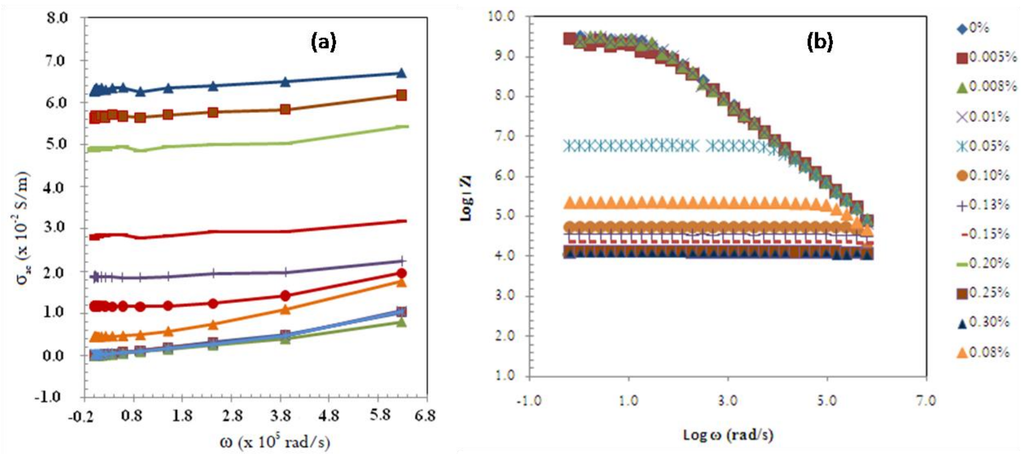


Fig. 4 (a) AC conductivity against angular frequency and (b) Impedance |Z| - frequency behaviour corresponding to different nanotube contents.

where σ_i is the matrix conductivity and σ_n the composite conductivity. Through curve fitting in the log-log plot of the conductivity at low nanotube contents, σ_i and *s* were estimated as 2.12 x 10^{-7} S/m and 0.75±0.06, respectively. The matrix conductivity obtained from linear regression curve fitting using equation (2) is close to the conductivity experimentally obtained for pristine epoxy resin samples, i.e., σ_{ac} = 2.68 x 10^{-7} S/m. The value of the *s* obtained is in agreement with expected values (0.8<s<1.0) which is indicative of a hopping in a disordered material where hopping charge carriers are subject to spatially randomly varying energy barriers (Kilbride, Coleman et al. 2002).

3.3 Impedance spectra analysis

The conductivity mechanisms in polymer/carbon filler (carbon black, synthetic graphite) based composites have been studied using equivalent circuit models (Wang, Pan et al. 2005). To understand the conductivity and its sensitivity to mechanical strain in current epoxy/MWCNT nanocomposites, a similar approach was used here. Fig. 5 presents the model of frequency dependence of the impedance modulus at the lowest point of the percolation region. At low CNT content, the CNTs are close but not in touch each other, with inter-tube gaps separating the individual CNTs and agglomerates. In the parallel resistor-capacitor model shown in Fig. 5, R_c is the contact resistance for the passage of electrons through the inter-tube distance, which can be approximated by a parallel-plate capacitor with area *A*, a separation distance d_s, and a capacitance $C=\varepsilon A/d_s$, where ε is the dielectric constant of the polymer. Each nanotube has a resistance R_a. A whole composite may be regarded as a similar equivalent circuit in which instead of *C*, R_c, and R_a equivalent series components of capacitance C_s, contact resistance (R_{cs}) and agglomerate resistance (R_{as}) are used to model the conduction via the CNTs network. Using circuit analysis theory, the resulting impedance of the composite is given by equation (3), and the real, imaginary and impedance modulus can be obtained. A plot of imaginary impedance against real impedance would give a semi circular curve about the real axis.

$$Z = R_{as} + \frac{R_{cs}}{1+\omega^2 R_{cs}^2 C_s^2} - j\frac{\omega R_{cs}^2 C_s}{1+\omega^2 R_{cs}^2 C_s^2} \quad \text{.......................................(3)}$$

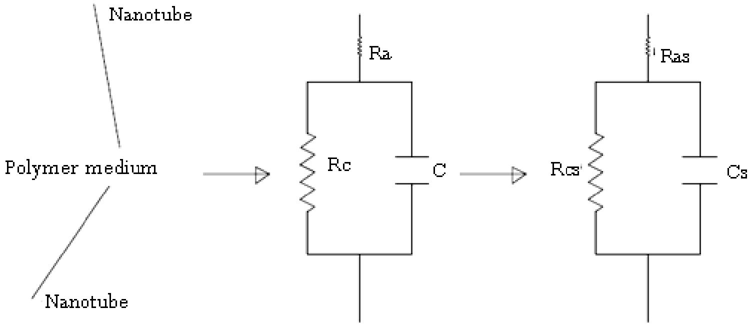


Fig. 5 Equivalent circuit model for low MWCNT loading nanocomposite

At low frequencies, flow of current through the capacitive gaps is impeded by the high reactance ($1/\omega C_s$) and is dominated by the impedance which is the sum of the series resistances R_{as} and R_{cs}. At intermediate frequencies, the reactance is lower than the contact resistance component R_{cs} and the current flows through the contact capacitance. As the frequency increases, the total impedance is largely determined by the reactance ($1/\omega C_s$) and decreases as the frequency increases. At high frequencies, the reactance decreases to a level where it is much lower than the nanotube or nanotube agglomerate resistance R_{as}, which now dominates the impedance. The total impedance at frequencies approaching 100kHz therefore tends towards a constant value equal to R_{as}, as shown in Fig. 6(a).

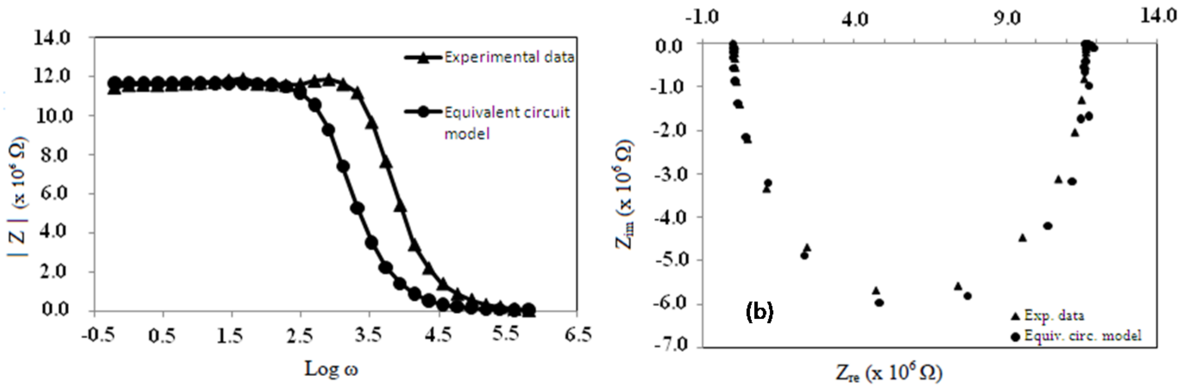


Fig. 6 (a) Impedance against angular frequency and imaginary impedance (Z_{im}) against real impedance (Z_{re}) at 0.05 %wt CNT.

The impedance modulus – frequency curve obtained by separating equation (3) into real and imaginary parts and solving for impedance modulus is also shown in Fig 7(a). Estimates of C_s, R_{as} and R_{cs} calculated from Fig. 6(a) are 8.11×10^{-11} F, 5.61×10^4 Ω and 1.16×10^7 Ω, respectively. Fig. 6(b) shows the experimental and predicted Z_{im} vs Z_{re}. According to the imaginary- real impedance relationship in equation (3), nearly semi-circular shaped curves are expected in Fig. 6(b). The good agreement between experimental measurements and predictions shown in Fig. 6 confirms that the parallel resistor-capacitor model can be used to investigate the conduction mechanisms in polymer-CNT nanocomposites close to the percolation threshold. More work to examine the effects of surface modification in CNTs and loading modes on the conduction mechanisms is currently underway.

4.0 CONCLUSIONS

Epoxy/multiwall carbon nanotubes nanocomposites with nanotube loading up to 0.3%wt were successfully prepared by simple shear mixing and curing process. Good dispersion of nanotubes in the epoxy matrix was observed. The nanocomposites followed the typical percolation power law with a percolation threshold of 0.055%wt CNT and a critical exponent t ≈ 1.14. Frequency independent AC conductivity was observed at low frequencies but not at high frequencies. It was confirmed that the equivalent circuit models can be used to predict the impedance response in these nanocomposites. At different carbon nanotube loading levels, parallel resistor-capacitor or series resistor-inductor equivalent circuit models can be used to investigate the effects of nanotube resistance, contact resistance and gap resistance on electrical behaviour of the nanocomposite.

5.0 REFERENCES

Anand, S. V. and D. R. Mahapatra (2009). Quasi-static and dynamic strain sensing using carbon nanotube/epoxy nanocomposite thin films. **18:** 045013-(13.

Bauhofer, W. and J. Z. Kovacs (2009). "A review and analysis of electrical percolation in carbon nanotube polymer composites." Composites Science and Technology **69**(10): 1486-1498.

Bumsuk Kim, M., M. Jongjin Lee and M. Insuk Yu (2003). "Electrical properties of single-wall carbon nanotube and epoxy composites." Journal of Applied Physics **94**: 6724-6728.

Hu, N., Z. Masuda, G. Yamamoto, H. Fukunaga, T. Hashida and J. Qiu (2008). "Effect of fabrication process on electrical properties of polymer/multi-wall carbon nanotube nanocomposites." Composites Part A: Applied Science and Manufacturing **39**: 893.

Kang, I., M. J. Schulz, J. H. Kim, V. Shanov and D. Shi (2006). "A carbon nanotube strain sensor for structural health monitoring." Smart Materials and Structures **15**(3): 737.

Kilbride, B. E., J. N. Coleman, J. Fraysse, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth and W. J. Blau (2002). "Experimental observation of scaling laws for alternating current and direct current conductivity in polymer-carbon nanotube composite thin films." Journal of Applied Physics **92**: 4024.

Kymakis, E. and G. A. J. Amaratunga (2002). "Single-wall carbon nanotube/conjugated polymer photovoltaic devices." Applied Physics Letters **80**: 112.

Li, J., P. C. Ma, W. S. Chow, C. K. To, B. Z. Tang and J.-K. Kim (2007). "Correlations between percolation threshold, dispersion state, and aspect ratio of carbon nanotubes." Advanced Functional Materials **17**: 3207-3215.

Li, N., Y. Huang, F. Du, X. He, X. Lin, H. Gao, Y. Ma, F. Li, Y. Chen and P. C. Eklund (2006). "Electromagnetic Interference (EMI) Shielding of Single-Walled Carbon Nanotube Epoxy Composites." Nano Letters **6**(6): 1141-1145.

McLachlan, D. S., C. Chiteme, C. Park, K. E. Wise, S. E. Lowther, P. T. Lillehei, E. J. Siochi and J. S. Harrison (2005). "AC and DC percolative conductivity of single wall carbon nanotube polymer composites." Journal of Polymer Science Part B: Polymer Physics **43**(22): 3273-3287.

Pham, G. T., Y.-B. Park, Z. Liang, C. Zhang and B. Wang (2008). "Processing and modeling of conductive thermoplastic/carbon nanotube films for strain sensing." Composites Part B: Engineering **39**(1): 209-216.

Sandler, J. K. W., J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer and A. H. Windle (2003). "Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites." Polymer **44**(19): 5893-5899.

Schmidt, R. H., I. A. Kinloch, A. N. Burgess and A. H. Windle (2007). "The effect of aggregation on the electrical conductivity of spin-coated polymer/carbon nanotube composite films." Langmuir **23**(10): 5707-5712.

Stauffer, D. (1985). Introduction to Percolation Theory. London, Taylor and Francis.

Wang, Y.-J., Y. Pan and Z. Xiang-Wu (2005). "Impedance Spectra of Carbon Black Filled High-Density Polyethylene Composites." Journal of Applied Polymer Science **98**: 1344-1350.

Yu, A., H. Hu, E. Bekyarova, M. E. Itkis, J. Gao, B. Zhao and R. C. Haddon (2006). "Incorporation of highly dispersed single-walled carbon nanotubes in a polyimide matrix." Composites Science and Technology **66**(9): 1190-1197.